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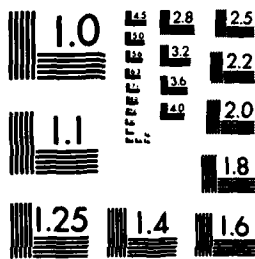
PHOTOPHYSICS OF POLYURETHANES BASED ON 17-NAPHTHALENE  
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Photophysics of Polyurethanes Based on 1,5-Naphthalene Diisocyanate

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by

C.E. Hoyle and K.J. Kim  
Department of Polymer Science  
University of Southern Mississippi  
Southern Station Box 10076  
Hattiesburg, MS 39406

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Photophysics of Polyurethanes based on  
1,5-Naphthalene Diisocyanate

Charles E. Hoyle and K. J. Kim

Department of Polymer Science  
University of Southern Mississippi  
Southern Station Box 10076  
Hattiesburg, MS 39406-0076

Introduction

Excimers are excited-state complexes formed between equivalent chemical species, one of which is in the excited state prior to forming the excimer. Over the past two decades, excimers in polymer systems have continued to attract a significant amount of attention. Key references may be found in a recent review by Guillet (1). With few exceptions, polymers with pendant chromophores, such as naphthyl or phenyl groups, readily form excimers which are characterized by their red-shifted (in comparison to emission from a single chromophore) emission spectra. In dilute solutions, the excimers result from intramolecular association of an excited aromatic chromophore and a ground state chromophore on the same polymer chain.

In contrast to the vast number of studies on excimers formed between aromatic chromophores pendant to the polymer backbone, relatively few papers have been published on excimers formed from polymers with the interactive species in the backbone. Selected examples can be found in references 2-5. In this paper, we report on the photophysical behavior of polyurethanes based on 1,5-naphthalene diisocyanate (NDI) which have naphthalene chromophores periodically spaced along the polymer backbone. Excimer formation is found in both dilute solutions and films. The discovery of the excimer emission in polyurethanes is of particular interest since excimer formation may alter the photolytic degradation process.

Experimental

The 1,5-naphthalene diisocyanate (NDI) was synthesized by reacting 1,5-diaminonaphthalene (Fluka) and trichloromethyl chloroformate (Fluka) in p-dioxane at the reflux temperature (100°C). The colorless solid (mp 126°C) was obtained by sublimation under vacuum. The propyl carbamate of 1-naphthyl isocyanate (mp 73°C) was prepared by reacting 1-naphthyl isocyanate (Aldrich) and 1-propanol (Baker) in ethyl acetate. The bispropyl carbamate of 1,5-naphthalene diisocyanate (mp 203°C) was prepared by reacting 1,5-naphthalene diisocyanate and 1-propanol in p-dioxane.

The NDI based polyurethanes were obtained by reacting 1,5-naphthalene diisocyanate and polytetramethylene oxide (MW 650 and 2000; Polysciences) with dibutyltin dilaurate and Dabco as catalysts in tetrachloroethane at 100°C for 2.5 hours. The polyurethanes formed were dissolved in dichloromethane and purified by double precipitation in cyclohexane. The molecular weight of NDI-650 and NDI-2000 were 51,000 and 63,000, respectively (GPC).

Emission spectra were recorded on a Perkin-Elmer 650-10S Fluorescence Spectrophotometer. Fluorescence decay data were obtained on a single-photon-counting apparatus from Photochemical Research Associates (PRA). The data were analyzed by a software package obtained from PRA based on the iterative convolution method. Infrared spectra were obtained on a Nicolet 5DX FTIR.

Results and Discussion

Before presenting the results for the NDI based polyurethanes, the emission characteristics of two small

molecule naphthyl carbamate models are reviewed. Figure 1 shows the steady-state fluorescence spectrum ( $\lambda_{ex} = 300$  nm) of a dilute solution ( $3.0 \times 10^{-4}$  M in benzene) of the bispropylcarbamate of NDI (1) with discernable peaks at 345 nm, 360 nm, and 375 nm. Excitation ( $\lambda_{ex} = 300$  nm) of a dilute solution ( $3.0 \times 10^{-4}$  M in benzene) of 1 yields a decay curve ( $\lambda_{em} = 350$  nm) which readily fits to a single exponential decay function with lifetime of 2.32 nsec. Similar emission characteristics were obtained for the propyl carbamate of 1-naphthyl isocyanate (2) with a single exponential decay time ( $\lambda_{ex} = 310$  nm,  $\lambda_{em} = 350$  nm) of 5.09 nsec. Fluorescence decay curves of 1 and 2 in dichloromethane where also single exponential giving lifetimes of 1.84 nsec and 3.59 nsec, respectively. In benzene, in which 2 but not 1 is highly soluble, concentrations of 2 above 1.55 M resulted in excimer formation as identified both by its characteristic red-shifted emission and long lived fluorescence lifetime (~21.7 nsec).

The steady state fluorescence spectrum (Figure 2) of a dilute dichloromethane solution (0.1 g/l) of a polyurethane designated as NDI-650 [based on 1,5-naphthalene diisocyanate (NDI) and a poly(tetramethylene oxide) polyol with average molecular weight of 650] is similar to that for the model biscarbamate (Figure 1). However, there is a distinctive red-shifted tail above 400 nm in the case of the NDI-650 polyurethane. Consistent with the red tail is the fact that the fluorescence decay curves of dilute solutions of NDI-650 cannot be fit to a single exponential decay function, no matter what the wavelength of observation. This suggests the possibility of excimer formation between two naphthyl chromophores on the same polymer chain (intramolecular). In order to affirm this postulation, the NDI-650 polyurethane fluorescence spectra were recorded in dilute solutions of solvents with decreased solvating power (poor solvents). As the solvent power decreases, the emission shifts to longer wavelengths as excimer formation becomes prominent. To illustrate this phenomenon, the fluorescence spectrum of NDI-650 in benzene (a poor solvent relative to dichloromethane) is given in Figure 3. It has both monomer (~350 nm) and excimer (>400 nm) emission. Support for assignment of the emission above 400 nm to an excimer state is provided by the excitation spectrum ( $\lambda_{em} = 430$  nm) of the red-shifted emission which is identical to the absorption spectrum of the NDI-650 polyurethane in benzene. Furthermore, the excimer is probably intramolecular since the concentration is significantly less than that observed for the onset of intermolecular excimer formation in several solvent systems. A preliminary analysis of the fluorescence decay curves of the NDI-650 polyurethane in benzene (0.1 g/l), was conducted. Attempts to fit the decay curve recorded at 330 nm to a sum of two exponentials failed. Fitting the decay curve to a sum of three exponentials, as recently suggested (6, 7), leads to acceptable results with lifetimes for the three exponentials of 1.3 nsec, 2.4 nsec and 22.3 nsec. Judging from the long lived portion ( $\tau = 22.3$  nsec) of the fluorescence decay curve recorded at 330 nm, it can be speculated that the excimer is probably formed reversibly and exists in dynamic equilibrium with an excited monomer species. A similar lifetime of 24.8 nsec was obtained from a second decay curve recorded at 500 nm (excimer emission) by fitting a single exponential decay function to the long lived portion of the decay curve. The short lived components (1.3 nsec and 2.4 nsec) from the decay curves recorded at 330 nm may arise from two monomeric species, one which is unquenched and one which is in equilibrium with the excimer, with different lifetimes. Such an approach to analysis of excimer kinetics has been employed (6, 7) to interpret the decay curves of other polymer systems.

Our basic interest in excimer formation in NDI-based polyurethanes lies in its effect on the photodegradation process, i.e., excimer formation could lead to a change in the mechanism for photolytic decomposition. With this in mind, it is of particular interest to note that the fluorescence spectrum of an NDI-650 polyurethane film

( $\lambda_{ex} = 300$  nm) is dominated by excimer emission (Figure 4). A preliminary multiexponential analysis of the decay curves indicates a complicated photophysical system. However, it can be reported that the long lived component of the excimer decay curve (taken at 500 nm) does yield a lifetime of  $\sim 22$  nsec for excimer emission, close to that obtained in benzene.

In contrast to the results for the NDI-650 polyurethane, the fluorescence spectrum of a polyurethane film of NDI-2000 [based on NDI and a poly(tetramethylene oxide) polyol with average molecular weight of 2,000] shows appreciable emission from the monomer component (Figure 5). Although the excimer and monomer decay curves are complex and difficult to analyze, the long lived component of the excimer decay curve (recorded at 500 nm) is about 21 nsec, in close agreement with the lifetime obtained for the NDI-650 film.

In contrasting the results for the NDI-650 and NDI-2000 films, it is apparent that the extent of excimer formation is greater for the NDI-650 film. It may be argued that the increased relative concentration of naphthyl carbamate chromophores in the NDI-650 film leads to increased excimer formation. It should, however, be pointed out that there is a distinct and perhaps critical structural difference between the NDI-650 and NDI-2000 polyurethane films which may manifest itself in increased excimer formation. In the NDI-650 polyurethane film, there is a significant degree of hydrogen bonding to the carbonyl on the urethane moiety. This is exemplified by the infrared spectra of the NDI-650 and NDI-2000 films given in Figure 5. The NDI-650 has primarily hydrogen bonded carbonyls ( $1,695\text{ cm}^{-1}$ ) while the NDI-2000 films have a high content of non-bonded carbonyls ( $1,740\text{ cm}^{-1}$ ). It is conceivable that the hydrogen bonding in the NDI-650 films may lock in or stabilize the excimer site geometry and provide for an increased degree of excimer, relative to monomer, fluorescence. This possibility is under investigation.

#### Conclusions

Fluorescence analysis, both steady-state and transient, indicates that excimer formation in polyurethanes based on 1,5-naphthalene diisocyanate is facile, both in dilute solution and solid films. The extent of excimer formation is directly related to the "poorness" of the solvent. In solution, a preliminary kinetic analysis indicates that the excimer is formed reversibly. For NDI-polyol based polyurethane films, steady-state fluorescence shows a difference in the ratio of excimer to monomer emission which depends on the length of the polyol segment. This difference could be due to hydrogen bonding of carbonyls in the urethane moiety, but additional work is required to confirm this postulation. Future work will concentrate on a more exact analysis of the decay curves for films and solutions of NDI based polyurethanes. In addition, the effect of excimer formation on the photodegradation properties will be investigated.

#### Acknowledgement

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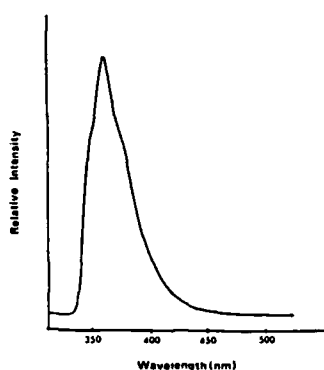


Fig. 1. Fluorescence spectrum of the bispropylcarbamate of NDI, ( $\lambda_{ex} = 300$  nm,  $3.0 \times 10^{-4}$  M in benzene).

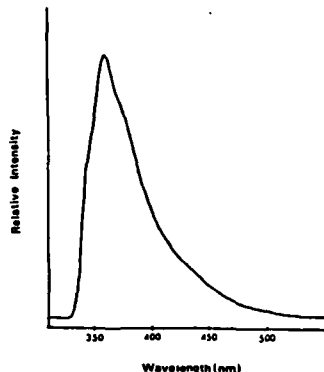


Fig. 2. Fluorescence spectrum of NDI-650 polyurethane in dichloromethane. ( $\lambda_{ex} = 300$  nm, 0.1 g/l).

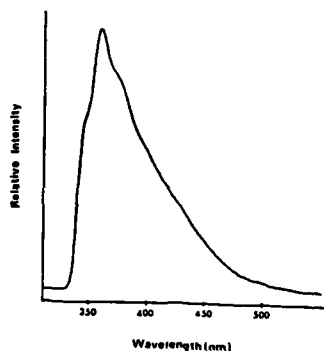


Fig. 3. Fluorescence spectrum of NDI-650 polyurethane in benzene. ( $\lambda_{ex} = 300$  nm, 0.1 g/l).

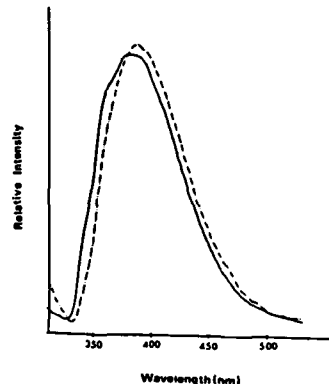


Fig. 4. Fluorescence spectra of the NDI-polyurethane films. ( $\lambda_{ex} = 300$  nm,) NDI-650 ——— NDI-2000 - - - - -.

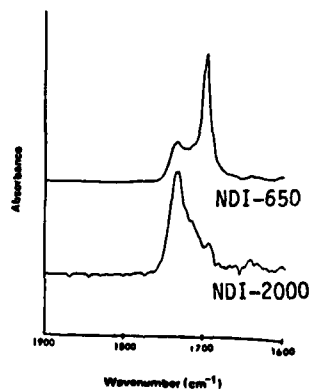


Fig. 5. Infrared spectra of the NDI polyurethane films.

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